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On the calculation of certain integrals occurring in the theory of molecules, especially three-centre and four-centre integrals

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By using a method involving expansion in spherical harmonics, it is shown that a general formula can be deduced for the potential integrals, which occur in the theory of molecules and crystals. Explicit formulæ are given for the two-centre, three-centre and four-centre integrals of atomic S-functions. The method can be applied to analytical wave functions, but the formulæ are more convenient for computations by means of numerical integration.

I. Introduction

In the theory of molecules and crystals the evaluation of certain integrals over products of atomic wave functions, particularly exchange integrals, three-centre and four-centre integrals, presents considerable difficulties. Integrals of these types have been treated by many authors, [1]—[30], but, as far as we know, any general way of investigating them has hitherto not been developed.

For analytical wave functions of the hydrogen-like type, all two-centre integrals can conveniently be evaluated by using elliptical coordinates, [2]—[17]. Some three-centre integrals have also been treated in this way, [14]—[17], but the results were here confined to some special configurations of the nuclei. A general formula for the three-centre integrals has not been given[1], and the four-centre integrals seem to have been neglected in a large part of the literature.[2]

The methods used here are certain expansions in spherical harmonics, first introduced by Coolidge [9] and later used extensively by Landshoff [22] and by Löwdin [19]. The purpose of this note is to show that these methods can easily be generalized to include all the potential integrals of the type considered here and that general formulæ can be deduced even for the three-centre and the four-centre integrals. Explicit formulæ will be given for S-functions.[3]

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[1] For some special cases see [9], [18] and [19].

[2] An approximate formula has been given by Sklar [28]; cf. also [29] and [30].

[3] The formula for the exchange integral given here, (24), was first deduced by Landshoff. The formulæ (23)—(28) were originally derived by the present authors independently of each other. Special cases of the formulæ for the three-centre integrals were already deduced by Coolidge in treating a molecular problem. The necessity of taking the terms corresponding to the three- and four-centre integrals of the type considered here into account in calculations of the cohesive energy of ionic crystals was shown by Fröman and Lundqvist Ark. f. fysik 2, N:o 40 (1950).

II. The general potential formula

Let us consider a potential integral of the general type

$$\int\int \frac{\Omega_1(1)\,\Omega_2(2)}{r_{12}}\,d\tau_1\,d\tau_2 \tag{1}$$

where $\Omega_1(\boldsymbol{r}_1)$ and $\Omega_2(\boldsymbol{r}_2)$ are arbitrary density functions, $d\tau_1$ and $d\tau_2$ are the volume elements, and r_{12} is the distance between the points 1 and 2. In order to evaluate (1) we will use the expansion of $1/r_{12}$ in spherical harmonics. If $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ are vectors from the same origin, α is the angle between them, and r_i and r_k denote the smallest and largest of the quantities r_1 and r_2, we have the expansion

$$\frac{1}{r_{12}} = \sum_{h=0}^{\infty} \frac{r_i^h}{r_k^{h+1}}\,P_h(\cos\alpha). \tag{2}$$

Introducing a fixed system of spherical polar coordinates (r, ϑ, φ), and using the addition theorem for the Legendre polynomials, we get

$$\frac{1}{r_{12}} = \sum_{h=0}^{\infty}\sum_{m=-h}^{+h} \frac{4\pi}{2h+1}\,\frac{r_i^h}{r_k^{h+1}}\,S_{hm}(1)\,S_{hm}^*(2), \tag{3}$$

where S_{hm} are the spherical harmonics, defined by

$$S_{hm}(\vartheta, \varphi) = k_{hm}\,P_h^m(\cos\vartheta)\,e^{im\varphi},\ \ k_{hm} = \sqrt{\frac{2h+1}{4\pi}\,\frac{(h-m)!}{(h+m)!}}. \tag{4}$$

They are orthonormalized and satisfy the relation

$$\int_0^{2\pi} d\varphi \int_0^{\pi} S_{hm}^*\,S_{h'm'}\sin\vartheta\,d\vartheta = \delta_{hh'}\,\delta_{m'm}. \tag{5}$$

Putting the expansion (3) into the integral (1), we obtain directly the general formula

$$\begin{aligned}
&\int\int \frac{\Omega_1(1)\,\Omega_2(2)}{r_{12}}\,d\tau_1\,d\tau_2 = \\
&\qquad = \sum_{h=0}^{\infty}\sum_{m=-h}^{+h}\frac{4\pi}{2h+1}\left\{\int_0^{\infty}\Omega_{1,h}^{m}(r_1)\cdot r_1^{-h+1}\,dr_1\int_0^{r_1}\Omega_{2,h}^{-m}(r_2)\cdot r_2^{h+2}\,dr_2 + \right. \\
&\left. + \int_0^{\infty}\Omega_{1,h}^{m}(r_1)\cdot r_1^{h+2}\,dr_1\int_{r_1}^{\infty}\Omega_{2,h}^{-m}(r_2)\cdot r_2^{-h+1}\,dr_2\right\} = \\
&\qquad = \sum_{h=0}^{\infty}\sum_{m=-h}^{+h}\frac{4\pi}{2h+1}\left\{\int_0^{\infty}\Omega_{1,h}^{m}(r_1)\cdot r_1^{-h+1}\,dr_1\int_0^{r_1}\Omega_{2,h}^{-m}(r_2)\cdot r_2^{h+2}\,dr_2 + \right. \\
&\left. + \int_0^{\infty}\Omega_{2,h}^{-m}(r_1)\cdot r_1^{-h+1}\,dr_1\int_0^{r_1}\Omega_{1,h}^{m}(r_2)\cdot r_2^{h+2}\,dr_2\right\}
\end{aligned} \tag{6}$$

where the last term has been transformed by using Dirichlet's formula for double integrals. The quantities $\Omega^{m}_{N,h}$ $(N = 1{,}2)$ are here given by the integral

$$\Omega^{m}_{N,h}(r) = \int_{0}^{2\pi} d\varphi \int_{0}^{\pi} \Omega_N(r\,\vartheta, \varphi)\, S_{hm}(\vartheta, \varphi) \sin\vartheta\, d\vartheta, \tag{7}$$

and they can therefore be interpreted as the coefficients of the expansion of Ω_N into spherical harmonics. Formula (6) forms the basis of our method of calculation.

III. Applications to two-centre, three-centre, and four-centre integrals of *S*-functions

In the theory of molecules and crystals, a fundamental integral is of the type

$$(\overset{\text{I}}{a}\;\overset{\text{II}}{b}\;\overset{\text{III}}{c}\;\overset{\text{IV}}{d}) = \int\!\!\int \frac{\overset{\text{I}}{\Psi}_a(1)\,\overset{\text{II}}{\Psi}_b(1)\,\overset{\text{III}}{\Psi}_c(2)\,\overset{\text{IV}}{\Psi}_d(2)}{r_{12}}\, d\tau_1\, d\tau_2, \tag{8}$$

where the indices a, b, c, d denote the different nuclei involved, and the Roman numerals indicate wave functions of various types. This integral is now a special case of the potential integral (1) with the density functions

$$\Omega_1 = \overset{\text{I}}{\Psi}_a\,\overset{\text{II}}{\Psi}_b, \qquad \Omega_2 = \overset{\text{III}}{\Psi}_c\,\overset{\text{IV}}{\Psi}_d, \tag{9}$$

and (8) can therefore be evaluated according to the general formula (6). For the sake of simplicity we will here confine ourselves to considering only S-functions, but we note that the method can be extended to include also P-functions and higher functions, even if, in the latter case, the calculations will be more complicated.

Let us choose the point a as the origin of our coordinate system (r, ϑ, φ), and let the vector $\boldsymbol{r}_{ac}$ represent the direction of the polar axis. Let the plane $\varphi = 0$ be determined by the vectors $\boldsymbol{r}_{ac}$ and $\boldsymbol{r}_{ab}$, and let further Φ be the angle between this plane and the plane determined by the vectors $\boldsymbol{r}_{ac}$ and $\boldsymbol{r}_{ad}$, i. e. $\varphi_d = \Phi$. The S-function Ψ_ν is spherically symmetrical around the nucleus ν $(\nu = a, b, c, d)$ and may here be defined by the expression

$$\Psi_\nu(1) = \frac{1}{\sqrt{4\pi}}\, g_\nu(r_{1\nu}). \tag{10}$$

According to (7) and (9) we obtain directly

$$\begin{aligned} \Omega^{m}_{1,h}(r_1) &= \frac{1}{4\pi}\int_{0}^{2\pi} d\varphi_1 \int_{0}^{\pi} \overset{\text{I}}{g_a}(r_{1a})\, \overset{\text{II}}{g_b}(r_{1b})\, S_{hm}(\vartheta_1, \varphi_1) \sin\vartheta_1\, d\vartheta_1, \\ \Omega^{-m}_{2,h}(r_2) &= \frac{1}{4\pi}\int_{0}^{2\pi} d\varphi_2 \int_{0}^{\pi} \overset{\text{III}}{g_c}(r_{2c})\, \overset{\text{IV}}{g_d}(r_{2d})\, S^{*}_{hm}(\vartheta_2, \varphi_2) \sin\vartheta_2\, d\vartheta_2. \end{aligned} \tag{11}$$

In order to evaluate the integrals (11), we will now expand the functions g_ν into spherical harmonics around the point a in the system (r, ϑ, φ), which for S-functions can be carried out in a simplified way. If $\vartheta_{N a \nu}$ denotes the angle between the vectors $\boldsymbol{r}_N$ and $\boldsymbol{r}_\nu$, we obtain at first the following expansion into Legendre polynomials

$$\left\{\begin{aligned} & g_\nu(r_{N\nu}) = \sum_{h=0}^{\infty} \alpha_h(r_{a\nu} \mid r_N)\, P_h(\cos\vartheta_{Na\nu}), && N = 1, 2 \\ & \alpha_h(r_{a\nu} \mid r_N) = \frac{2h+1}{2} \int_0^\pi g_\nu(r_{N\nu})\, P_h(\cos\vartheta_{Na\nu}) \sin\vartheta_{Na\nu}\, d\vartheta_{Na\nu}. && \end{aligned}\right. \tag{12}$$

For $\nu = b$, c, and d we then get the expansions into spherical harmonics

$$\begin{aligned} \overset{\text{II}}{g}_b(r_{1b}) &= \sum_{h=0}^{\infty} \sum_{m=-h}^{+h} \frac{4\pi}{2h+1} \overset{\text{II}}{\alpha}_h(r_{ab} \mid r_1)\, S_{hm}(b)\, S_{hm}^{*}(\vartheta_1, \varphi_1), \\ \overset{\text{III}}{g}_c(r_{2c}) &= \sum_{h=0}^{\infty} \overset{\text{III}}{\alpha}_h(r_{ac} \mid r_2)\, P_h(\cos\vartheta_2), \\ \overset{\text{IV}}{g}_d(r_{2d}) &= \sum_{h=0}^{\infty} \sum_{m=-h}^{+h} \frac{4\pi}{2h+1} \overset{\text{IV}}{\alpha}_h(r_{ad} \mid r_2)\, S_{hm}^{*}(d)\, S_{hm}(\vartheta_2, \varphi_2), \end{aligned} \tag{13}$$

where, in the cases $\nu = b$ and $\nu = d$, we have used the addition theorem for the Legendre polynomials. Putting these expansions into the integrals (11) and using the relation (5), we obtain the following explicit expressions

$$\Omega_{1,h}^{m}(r_1) = \left\{\begin{aligned} & \frac{k_{hm}}{2h+1} P_h^m(\cos\vartheta_{bac})\, \overset{\text{I}}{g}_a(r_1)\, \overset{\text{II}}{\alpha}_h(r_{ab} \mid r_1), && b \neq \begin{cases} a \\ c \end{cases} \\ & \frac{k_{hm}}{2h+1} \delta_{m0}\, \overset{\text{I}}{g}_a(r_1)\, \overset{\text{II}}{\alpha}_h(r_{ab} \mid r_1), && b = c \\ & \frac{k_{hm}}{2h+1} \delta_{m0}\, \delta_{h0}\, \overset{\text{I}}{g}_a(r_1)\, \overset{\text{II}}{g}_a(r_1), && b = a \end{aligned}\right. \tag{14}$$

and

$$\Omega_{2,h}^{-m}(r_2) = \left\{\begin{aligned} & \sum_{l=0}^{\infty} \frac{k_{hm}}{2h+1} \frac{(l-m)!}{(l+m)!} P_l^m(\cos\vartheta_{cad})\, e^{-im\Phi}\, \overset{\text{IV}}{\alpha}_l(r_{ad} \mid r_2)\, \overset{\text{III}}{\alpha}{}_{l,h}^{m}(r_{ac} \mid r_2) && d \neq \begin{cases} a \\ c \end{cases} \\ & \frac{k_{hm}}{2h+1} \delta_{m0}\, \overset{\text{III, IV}}{\alpha}_h(r_{ac} \mid r_2), && d = c \\ & \frac{k_{hm}}{2h+1} \delta_{m0}\, \overset{\text{III}}{\alpha}_h(r_{ac} \mid r_2)\, \overset{\text{IV}}{g}_a(r_2). && d = a \end{aligned}\right. \tag{15}$$

In addition to (12), we have here used the notations

$$\begin{aligned} \overset{\text{III, IV}}{\alpha_h}(r_{ac}\,|\,r_2) &= \frac{2h+1}{2}\int_0^\pi \overset{\text{III}}{g_c}(r_{2c})\,\overset{\text{IV}}{g_c}(r_{2c})\,P_h(\cos\vartheta_2)\sin\vartheta_2\,d\vartheta_2, \\ \overset{\text{III}}{\alpha^m_{l,h}}(r_{ac}\,|\,r_2) &= \frac{2h+1}{2}\int_0^\pi \overset{\text{III}}{g_c}(r_{2c})\,P_l^m(\cos\vartheta_2)\,P_h^m(\cos\vartheta_2)\sin\vartheta_2\,d\vartheta_2. \end{aligned} \tag{16}$$

The main problem is now the calculation of the radial functions $\alpha(r)$ defined by (12) and (16). Let us first treat the integral in the right-hand member of (12). Following Löwdin, [19], p. 19, we will introduce the new integration variable $r_{N\nu} = R$, which gives

$$\begin{aligned} R^2 &= r_{a\nu}^2 + r_N^2 - 2\,r_N\,r_{a\nu}\cos\vartheta_{Na\nu}, \\ \sin\vartheta_{Na\nu}\,d\vartheta_{Na\nu} &= \frac{R}{r_N\,r_{a\nu}}\,dR, \end{aligned} \tag{17}$$

and

$$\alpha_h(r_{a\nu}\,|\,r) = \frac{2h+1}{2\,r\,r_{a\nu}}\int_{|r_{a\nu}-r|}^{r_{a\nu}+r} g_\nu(R)\,P_h\left(\frac{r^2+r_{a\nu}^2-R^2}{2\,r\,r_{a\nu}}\right)\cdot R\,dR. \tag{18}$$

For $h = 0, 1, \ldots$ we obtain in particular

$$\begin{aligned} \alpha_0(r_{a\nu}\,|\,r) &= \frac{1}{2\,r\,r_{a\nu}}\int_{|r_{a\nu}-r|}^{r_{a\nu}+r} g_\nu(R)\,R\,dR, \\ \alpha_1(r_{a\nu}\,|\,r) &= \frac{3}{4\,r^2\,r_{a\nu}^2}\left\{(r^2+r_{a\nu}^2)\int_{|r_{a\nu}-r|}^{r_{a\nu}+r} g_\nu(R)\,R\,dR - \int_{|r_{a\nu}-r|}^{r_{a\nu}+r} g_\nu(R)\,R^3\,dR\right\}, \end{aligned} \tag{19}$$

. . . .

More complete formulae may be found in Löwdin, [19], p. 20—21. This means that the radial functions $\alpha_h(r_{a\nu}\,|\,r)$ can be easily calculated from the functions $g_\nu(r)$, whether the latter are given analytically or numerically. The formulae (19) are, in fact, particularly suitable for computations using numerical integrations.

We note that the corresponding formulae for $\overset{\text{III, IV}}{\alpha_h}(r_{ac}\,|\,r)$ may be obtained by putting the product $\overset{\text{III}}{g_c}\,\overset{\text{IV}}{g_c}$ instead of g_ν into the relations (18) and (19).

Finally, we have to treat the integral (16″). Putting the expansion (13″) into (16″), we get at once the formula

$$\overset{\text{III}}{\alpha^m_{l,h}}(r_{ac}|r_2) = \frac{2h+1}{2}\sum_k \Lambda^m_{lh,k}\,\overset{\text{III}}{\alpha_k}(r_{ac}|r_2) \tag{20}$$

with

$$\Lambda^m_{lh,k} = \int_{-1}^{+1} P^m_l(u)\,P^m_h(u)\,P_k(u)\,du, \tag{21}$$

The coefficients $\Lambda^m_{lh,k}$ may be found by using the elementary rules in the theory of the spherical harmonics; the first few of them are

$$\begin{aligned}
\Lambda^m_{lh,0} &= \frac{1}{2\pi k^2_{lm}}\,\delta_{hl}, \quad \Lambda^0_{l0,k} = \frac{2}{2l+1}\,\delta_{lk},\\
\Lambda^0_{l1,k} &= \frac{2}{2l+1}\left\{\frac{l+1}{2l+3}\,\delta_{l+1,k} + \frac{l}{2l-1}\,\delta_{l-1,k}\right\},\\
\Lambda^1_{l1,k} &= \frac{2l(l+1)}{2l+1}\left\{\frac{1}{2l-1}\,\delta_{l-1,k} + \frac{1}{2l+3}\,\delta_{l+1,k}\right\},\\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots
\end{aligned} \tag{22}$$

Other quantities of this type can easily be calculated by means of the formulae for products of spherical harmonics[1] given by Coolidge, [9], p. 204—206. Hence, all the functions $\alpha(r)$ can be found by means of the elementary functions given by (18) and (19).

Combining (14) and (15) with the fundamental formula (6), we can now obtain explicit expressions for all two-centre, three-centre, and four-centre integrals of the type (8) involving only S-functions:

Two-centre integrals:

$$\begin{aligned}
(\overset{\text{I}}{a}\,\overset{\text{II}}{a}\,\overset{\text{III}}{c}\,\overset{\text{IV}}{c}) = &\int_0^\infty \overset{\text{III,IV}}{\alpha_0}(r_{ac}|r_1)\,r_1\,dr_1\int_0^{r_1}\overset{\text{I}}{g_a}(r_2)\,\overset{\text{II}}{g_a}(r_2)\,r_2^2\,dr_2 +\\
&+\int_0^\infty \overset{\text{III,IV}}{\alpha_0}(r_{ac}|r_1)\,r_1^2\,dr_1\int_{r_1}^\infty \overset{\text{I}}{g_a}(r_2)\,\overset{\text{II}}{g_a}(r_2)\,r_2\,dr_2 .
\end{aligned} \tag{23}$$

$$\begin{aligned}
(\overset{\text{I}}{a}\,\overset{\text{II}}{c}\,\overset{\text{III}}{c}\,\overset{\text{IV}}{a}) = \sum_{h=0}^\infty \frac{1}{(2h+1)^2}\Bigg\{&\int_0^\infty \overset{\text{I}}{g_a}(r_1)\,\overset{\text{II}}{\alpha_h}(r_{ac}|r_1)\,r_1^{-h+1}\,dr_1\int_0^{r_1}\overset{\text{IV}}{g_a}(r_2)\,\overset{\text{III}}{\alpha_h}(r_{ac}|r_2)\,r_2^{h+2}\,dr_2 +\\
&+\int_0^\infty \overset{\text{IV}}{g_a}(r_1)\,\overset{\text{III}}{\alpha_h}(r_{ac}|r_1)\,r_1^{-h+1}\,dr_1\int_0^{r_1}\overset{\text{I}}{g_a}(r_2)\,\overset{\text{II}}{\alpha_h}(r_{ac}|r_2)\,r_2^{h+2}\,dr_2\Bigg\}.
\end{aligned} \tag{24}$$

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[1] For the case $l=h$, see also H. Bethe, Ann. d. Phys. *3*, 133 (1929), particularly p. 188—192.

$$\left(\overset{\mathrm{I}}{a}\,\overset{\mathrm{II}}{a}\,\overset{\mathrm{III}}{c}\,\overset{\mathrm{IV}}{a}\right) = \int_0^\infty \overset{\mathrm{IV}}{g_a}(r_1)\,\overset{\mathrm{III}}{\alpha_0}(r_{ac}|r_1)\,r_1\,dr_1 \int_0^{r_1} \overset{\mathrm{I}}{g_a}(r_2)\,\overset{\mathrm{II}}{g_a}(r_2)\,r_2^2\,dr_2 + \int_0^\infty \overset{\mathrm{IV}}{g_a}(r_1)\,\overset{\mathrm{III}}{\alpha_0}(r_{ac}|r_1)\,r_1^2\,dr_1 \int_{r_1}^\infty \overset{\mathrm{I}}{g_a}(r_2)\,\overset{\mathrm{II}}{g_a}(r_2)\,r_2\,dr_2. \tag{25}$$

Three-centre integrals:

$$\left(\overset{\mathrm{I}}{a}\,\overset{\mathrm{II}}{a}\,\overset{\mathrm{III}}{c}\,\overset{\mathrm{IV}}{d}\right) = \sum_{h=0}^{\infty} \frac{1}{2h+1} P_h(\cos\vartheta_{cad}) \cdot \left\{ \int_0^\infty \overset{\mathrm{III}}{\alpha_h}(r_{ac}|r_1)\,\overset{\mathrm{IV}}{\alpha_h}(r_{ad}|r_1)\,r_1\,dr_1 \int_0^{r_1} \overset{\mathrm{I}}{g_a}(r_2)\,\overset{\mathrm{II}}{g_a}(r_2)\,r_2^2\,dr_2 + \int_0^\infty \overset{\mathrm{III}}{\alpha_h}(r_{ac}|r_1)\,\overset{\mathrm{IV}}{\alpha_h}(r_{ad}|r_1)\,r_1^2\,dr_1 \int_{r_1}^\infty \overset{\mathrm{I}}{g_a}(r_2)\,\overset{\mathrm{II}}{g_a}(r_2)\,r_2\,dr_2 \right\}. \tag{26}$$

$$\left(\overset{\mathrm{I}}{a}\,\overset{\mathrm{II}}{b}\,\overset{\mathrm{III}}{c}\,\overset{\mathrm{IV}}{a}\right) = \sum_{h=0}^{\infty} \frac{1}{(2h+1)^2} P_h(\cos\vartheta_{bac}) \cdot \left\{ \int_0^\infty \overset{\mathrm{I}}{g_a}(r_1)\,\overset{\mathrm{II}}{\alpha_h}(r_{ab}|r_1)\,r_1^{-h+1}\,dr_1 \int_0^{r_1} \overset{\mathrm{III}}{\alpha_h}(r_{ac}|r_2)\,\overset{\mathrm{IV}}{g_a}(r_2)\,r_2^{h+2}\,dr_2 + \int_0^\infty \overset{\mathrm{III}}{\alpha_h}(r_{ac}|r_1)\,\overset{\mathrm{IV}}{g_a}(r_1)\,r_1^{-h+1}\,dr_1 \int_0^{r_1} \overset{\mathrm{I}}{g_a}(r_2)\,\overset{\mathrm{II}}{\alpha_h}(r_{ab}|r_2)\,r_2^{h+2}\,dr_2 \right\}. \tag{27}$$

Four-centre integrals: $(\varepsilon_0 = 1,\ \varepsilon_m = 2\ \ m \geq 1)$

$$\left(\overset{\mathrm{I}}{a}\,\overset{\mathrm{II}}{b}\,\overset{\mathrm{III}}{c}\,\overset{\mathrm{IV}}{d}\right) = \sum_{h=0}^{\infty}\sum_{l=0}^{\infty}\sum_{m=0}^{+h} \frac{\varepsilon_m}{(2h+1)^2}\,\frac{(h-m)!\,(l-m)!}{(h+m)!\,(l+m)!} P_h^m(\cos\vartheta_{bac})\,P_l^m(\cos\vartheta_{dac})\cos m\Phi \cdot \left\{ \int_0^\infty \overset{\mathrm{I}}{g_a}(r_1)\,\overset{\mathrm{II}}{\alpha_h}(r_{ab}|r_1)\,r_1^{-h+1}\,dr_1 \int_0^{r_1} \overset{\mathrm{III}}{\alpha_{hl}^m}(r_{ac}|r_2)\,\overset{\mathrm{IV}}{\alpha_l}(r_{ad}|r_2)\,r_2^{h+2}\,dr_2 + \int_0^\infty \overset{\mathrm{III}}{\alpha_{hl}^m}(r_{ac}|r_1)\,\overset{\mathrm{IV}}{\alpha_l}(r_{ad}|r_1)\,r_1^{-h+1}\,dr_1 \int_0^{r_1} \overset{\mathrm{I}}{g_a}(r_2)\,\overset{\mathrm{II}}{\alpha_h}(r_{ab}|r_2)\,r_2^{h+2}\,dr_2 \right\}. \tag{28}$$

Finally we will remark that another important molecular integral, the three-center integral

$$\int \Psi_a(1)\,\Psi_b(1)\,F_c(1)\,d\tau_1 \tag{29}$$

has been treated by means of the same method by Löwdin [19], p. 41—43.

IV. Comments

In this paper we have deduced a general potential formula, which has been applied to some two-centre, three-centre, and four-centre integrals of S-functions. These formulae, (23)—(28), are particularly suitable for computations by means of numerical integrations if the start functions $g(r)$ are given numerically, either in the form of Hartree-Fock functions or in the form of tabulated analytical functions. In general, the convergency of the infinite series in h is rather good; in practical applications to molecules and crystals, we have found it sufficient to take only the terms corresponding to $h = 0, 1, 2,$ and 3 into account.[1]

Finally, we wish to point out that, in treating the cohesive energy of crystals or molecules having a high degree of symmetry, considerable simplifications can sometimes be performed by summing the contributions from the three-centre and four-centre integrals over suitable configurations of the nuclei involved. A very simple method of treating such symmetrical problems has been developed by one of us (P. O. L.) and will be published elsewhere.

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REFERENCES. [1] **W. Heitler—F. London,** Z. f. Phys. **44,** 455 (1927). — [2] **Y. Sugiura,** Z. f. Phys. **45,** 484 (1927). — [3] **E. C. Kemble—C. Zener,** Phys. Rev. **33,** 512 (1929). — [4] **C. Zener—V. Guillemin,** Phys. Rev. **34,** 999 (1929). — [5] **J. H. Bartlett,** Phys. Rev. **37,** 506 (1931). — [6] **J. H. Bartlett—W. H. Furry,** Phys. Rev. **38,** 1615 (1931). — [7] **N. Rosen,** Phys. Rev. **38,** 225 (1931). — [8] **J. Podolanski,** Ann. d. Phys. **10,** 868 (1931). — [9] **A. S. Coolidge,** Phys. Rev. **42,** 189 (1932). — [10] **H. M. James—A. S. Coolidge,** J. Chem. Phys. **1,** 825 (1933). — [11] **M. Goeppert—Mayer—A. L. Sklar,** J. Chem. Phys. **6,** 645, (1938). — [12] **A. L. Sklar—R. H. Lyddane,** J. Chem. Phys. **7,** 374 (1939). — [13] **V. Griffing,** J. Chem. Phys. **15,** 421 (1947). — [14] **J. Hirschfelder—H. Eyring—N. Rosen,** J. Chem. Phys. **4,** 121 (1936). — [15] **J. Hirschfelder—H. Diamond—H. Eyring,** J. Chem. Phys. **5,** 695 (1937). — [16] **D. Stevenson—J. Hirschfelder,** J. Chem. Phys. **5,** 933 (1937). — [17] **J. Hirschfelder—O. Weygandt,** J. Chem. Phys. **6,** 806 (1938). — [18] **C. A. Coulson,** Proc. Cambridge Phil. Soc. **31,** 244 (1935) and **33,** 104 (1937). — [19] **P. O. Löwdin,** "A Theoretical Investigation into some Properties of Ionic Crystals", Thesis, Uppsala 1948. — [20] **M. Delbrück,** Ann. d. Phys. **5,** 36 (1930). — [21] **F. Hund,** Die Physik **1**:4, 163 (1933). — [22] **R. Landshoff.** Z. f. Phys. **102,** 201 (1936). — [23] **P. Gombás,** Z. f. Phys. **116,** 184 (1940). — [24] **C. A. Coulson,** Proc. Cambridge Phil. Soc. **38,** 210 (1942). — [25] **R. S. Mulliken,** Phys. Rev. **74,** 736 (1948). — [26] **R. G. Parr—B. L. Crawford,** J. Chem. Phys. **16,** 1049 (1948). — [27] **R. S. Mulliken—C. A. Rieke—D. Orloff—H. Orloff,** J. Chem. Phys. **17,** 1248 (1949). — [28] **A. L. Sklar,** J. Chem. Phys. **7,** 984 (1939). — [29] **A. London,** J. Chem. Phys. **13,** (1945). — [30] **R. S. Mulliken,** J. Chimie Physique **46,** 497, 675 (1949).

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[1] See, for instance, table (25.4) in Löwdin, [19], p. 79.

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